

EFFECT OF HUMIDITY DURING MANUFACTURING ON THE INTERFACIAL STRENGTH OF NON-PRE-DRIED FLAX FIBRE/ UNSATURATED POLYESTER COMPOSITES

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Abstract

The influence of moisture content in the environment during manufacture of a novel cobalt-free UP matrix reinforced with flax fibres, on the fibre-matrix adhesion was studied. Flax surface energy was experimentally determined by measuring contact angles on technical fibres, using the Wilhelmy technique and the acid-base theory. The mechanical strength of the interface under different humidity conditions was characterized by the critical local value of interfacial shear stress, τ_d , at the moment of crack initiation, which was assessed by single-fibre pull-out tests. Differential scanning calorimetry and x-ray photoelectron spectroscopy analysis gave further insight into the topic. The results suggest that the effect of humidity during manufacturing on the composite interface might be limited. However, longitudinal composite strength decreased somewhat for composites produced in humid conditions, showing that there is some detrimental effect of high levels of moisture during cure on the fibre mechanical performance, likely caused by some fibre degradation.

Keywords: A. Natural-Fibers; B. Interface/Interphase; C. Micro-mechanics; D. Cure

1. INTRODUCTION

Considerable research has been devoted to natural plant fibres (such as flax, hemp, jute, bamboo, coir, etc.) as reinforcing element for composite materials due to their renewable nature and excellent mechanical properties [1, 2]. These properties depend mainly on the structure and chemical composition of the fibre.

Plant fibres are composed of cellulose, hemicelluloses, lignin, pectin, and extractives. While cellulose is the reinforcing material ensuring the rigidity and strength of the plant fibre, lignin and hemicelluloses form the matrix which holds the cells (elementary fibres) together and is the medium for stress transfer. Hemicelluloses contribute to the integrity of the elementary fibres by interacting with cellulose and, in some specific cases, with lignin [3]. Pectin content in plant fibres is often very low, but they are strategically located within the structure of plant cell walls contributing to tissue integrity and rigidity [3, 4]. Finally, extractives are a mixture of small molecular weight individual compounds such as fats, waxes, and phenolic constituents [5]. Most of them are easily removed during fibre extraction processes, but even a very small amount remaining on the fibre surface can affect the interfacial properties of composites reinforced with plant fibres [6].

Natural fibres inevitably interact with water present in the air. When moisture reaches the fibre, the hydrogen bonds break and hydroxyl groups form new hydrogen bonds with water molecules [5]. This not only may affect the internal structure and the mechanical properties of the natural fibre reinforcement [7], but may also alter the fibre surface chemical composition, which is more exposed to the environment. The reduction of mechanical properties of natural fibre composites is typically attributed to the inherent interaction of natural fibres with water, which may lead to damage at the interface [8, 9]. Therefore, several reports conclude that natural fibres need to be dried before matrix impregnation, and that the composite manufacturing should be performed under controlled humidity conditions [8, 10].

However, matrices can also be affected by moisture and water content, which can deteriorate the curing process as in the case of unsaturated polyester (UP) resins [11, 12]. The latter are cured via radical mechanisms by making use of a curing system, which is usually composed of organic peroxide (MEKP) as radical initiator and cobalt carboxylate (“cobalt”) as accelerator. These two components react and start to generate radicals which in turn react with the styrene and the UP to form a 3D network. However, cobalt is susceptible to hydrolysis under the presence of water, becoming unreactive for the curing process. The curing system has a great influence on the quality of the cured product and the speed and ease of the curing process [12].

The aim of this article is to study the influence of moisture content in the environment (affecting fibre and matrix) during manufacture of cobalt-free UP matrix reinforced with flax fibres, on the mechanical properties of their composites. A new copper based UP resin accelerator developed by AkzoNobel is presented, which shows very low sensitivity to presence of water during cure. This means that natural fibres when processed with this resin system would not need to be dried anymore, which obviously will save energy and cost. The fibre surface physical interactions were analysed by measuring contact angles with different test liquids and at different humidity conditions. The fibre surface chemical composition was analysed by X-ray photoelectron spectroscopy (XPS). These results were contrasted with those obtained by single fibre pull-out and 3 point bending (3PBT) tests, to evaluate the mechanical adhesion strength.

2. MATERIALS AND METHODS

2.1 Materials

Long unidirectional flax mats (FlaxTape 200) were obtained from Lineo. The technical fibres used for pull-out tests were manually extracted from this mat.

Ultrapure water (18.2 Ω cm resistivity) from Millipore, and ethylene glycol and diiodomethane from Merck were used to study the fibres' wetting behaviour.

The UP resin (Synolite 1967-N-1), peroxide curing agent (Butanox M-50), accelerator (Nouryact CF-32), and inhibitor (NLC-10) were provided by AkzoNobel. The proportions of curing agent and accelerator used in this research were 1.5 and 1.0 phr (parts per hundred) respectively for the preparation of pull-out samples. For the manufacturing of composites, the same proportions were used plus 0.1 phr of inhibitor, to slow down the reaction for larger volumes.

2.2 Materials preparation

Technical flax fibres were cleaned with warm water for one hour (90°C), then wiped with ethanol with a piece of cotton tissue before being dried in a vacuum oven at 80°C for one hour. The fibres were then separated in 4 groups and conditioned at 0%, 50%, 70%, and 100% RH (20°C) in a climate chamber for 24 hours before contact angle measurements. The same room conditions were kept during contact angle measurement.

The fibres for single fibre pull-out tests were separated in 3 groups and conditioned at 0%, 50% and 70% RH (80°C), in a climate chamber for 24 hours prior to the preparation of the pull-out test samples. Samples were prepared at 50% RH (20°C), which are the controlled climate conditions of our lab, but conditioned samples were submersed immediately in the mixed resin formulation. They were then exposed to standard lab conditions for no more than 10 minutes (period needed for the UP resin to cure), and introduced again to the climate chamber at 0%, 50%, 70% RH (80°C) for post-curing and acclimatization during 2 hours. Finally the samples were stored at 50% RH (20°C) for 24 hours and the pull-out tests were performed under the same room conditions. Additionally, a group of fibres were conditioned at 50% RH (80°C), post-cured at 0% RH (80°C) during 2 hours and stored at 50% RH (20°C) for 24 hours before pull-out test, in order to study the effect of shrinkage due to humidity loss.

Two groups of unidirectional mats were conditioned at 0% and 100% RH during 1 week (20°C) for 3 point bending tests. The composites were manufactured at room conditions (50% RH, 20°C) using vacuum assisted resin infusion. Once the composites were consolidated, these were acclimatized (50%

RH, 20°C) during 24 hours before 3PBT, and another group during 6 months in order to evaluate a possible aging effect. The tests were performed at 50% RH (20°C).

2.3 Contact angle measurements and surface energy analysis

Advancing and receding contact angles of various test liquids were measured on the technical flax fibres under controlled conditions (see section 2.2), with a Krüss K100 tensiometer using the Wilhelmy technique [6, 13]. The selection of water, diiodomethane, and ethylene glycol as test liquids is based on the difference of surface energy components between them (water is presumed predominantly acidic, ethylene glycol is basic, and diiodomethane is a non-polar liquid), according to the Van Oss model [14] and the scale proposed by Della Volpe [15].

Surface energy components were calculated according to the Van Oss model and by using the SurfTen 4.3 software developed by Claudio Della Volpe [15]. The complete description of the methodology for measuring the fibre perimeter and the calculation of contact angles is described in a previous publication [13].

2.4 Gel time and peak exothermic temperature

UP resin sample volumes of 30 mL were used for the test under room conditions (50% RH, 20°C). The ASTM D2471 test method was used as reference.

2.5 Differential scanning calorimetry (DSC)

A differential scanning calorimetry (DSC) test was performed with a DSC Q2000 T.A. equipment, in order to study the curing and post-curing process of the UP resin.

2.6 Surface characterization: X-ray photoelectron spectroscopy (XPS)

XPS analyses were performed on a Kratos Axis Ultra spectrometer (Kratos Analytical – Manchester – UK) equipped with a monochromatized aluminium X-ray source (powered at 10 mA and 15 kV). More information regarding the XPS analysis procedure can be found in our previous publication [13].

2.7 Pull-out test

2.7.1 Sample preparation: A technical flax fibre, conditioned according to section 2.2, is fixed between two silicon blocks and stretched with the help of an adhesive tape according to Figure 1 - Left. A ring is placed on the silicon blocks in such a way that the fibre is located in its centre (see Figure 1 - Left). After the fibre is placed, UP liquid resin is added inside the ring. In this manner, the fibre is located in the centre and perpendicular to the surface of the cylindrical polymer block once the resin is solidified. The number of rings controls the embedded length.

To perform the pull-out test, the block of polymer and the fibre is attached to the load cell of an Instron 5943 mini tensile machine. It is important to carefully position the block of polymer since the area where the blades touch the upper surface of the block plays an important role concerning the induced compressive stress profile in the specimen. This is done with the help of an optical microscope to guarantee accuracy. A fibre free length of 5 mm was chosen for all the specimens.

2.7.2 Evaluation of the interfacial strength: The fibre matrix interfacial bond strength was characterized by the critical local value of interfacial shear stress, τ_d [16]. This is defined as the stress at which local debonding of the fibre from the matrix takes place. At this stage the recorded force will continue increasing since the crack growth is stabilised by the friction between fibre and matrix in the debonded area (interfacial friction, τ_f), until the crack becomes unstable at a finite crack length, a , and the total debonding of the fibre from the matrix occurs at F_{max} (see Figure 1 - Right).

In the force-displacement curve (Figure 1 - Right), the visible 'kink' corresponds to the start of debonding at the interface or crack initiation. This crack propagates along the interface while the pull-out force increases and the fibre slides out from the matrix, with friction acting between the recently debonded surfaces. Accordingly, the debond force is the key parameter to characterize the strength of a fibre-matrix system. However, since this debond force is difficult to determine, the only reliable measured load value is F_{max} .

The estimation of τ_d and τ_f was performed following the model developed by Zhandarov et al. [16, 17], which is based on the shear lag model of stress transfer to the matrix, and assumes that for any current crack length, a , the shear stress at the crack tip, $\tau_{(a)}$, is constant ($\tau_{(a)} = \tau_d = \text{const}$). Accordingly, the current applied force during a pull-out test (F), can be described as a function of the crack length, a .

$$F = \frac{\pi d}{\beta} \left\{ \tau_d \tanh[\beta(l_e - a)] - \tau_T \tanh[\beta(l_e - a)] \tanh\left[\frac{[\beta(l_e - a)]}{2}\right] + \beta a \tau_f \right\} \quad (1)$$

Where τ_T is the residual stress due to thermal shrinkage, τ_f is the frictional stress in the already debonded region, and β is the corrected shear-lag parameter according to Naim [18].

τ_T is defined as,

$$\tau_T = \frac{\beta r_f E_f}{2} (\alpha_f - \alpha_m) \Delta T \quad (2)$$

Where E_f is the longitudinal tensile modulus of the fibre, r_f is the radius of the fibre, α_f and α_m are the longitudinal coefficients of thermal expansion (CTE) of the fibre and the matrix respectively, and ΔT is the difference between the test temperature and the stress-free temperature during composite production.

The total debonding of the fibre from the matrix occurs at the recorded peak force F_{max} (see Figure 1 - Right). The force up to that moment reflects a combined resistance from friction in already debonded areas and adhesion in the still adhered section. The value of F_{max} can be used to obtain τ_d and τ_f by fitting experimental data according to the algorithm developed by Zhandarov et al. [19], and by using our own built code in Python language.

2.8 Flexural test (3PBT)

Unidirectional composites were prepared by vacuum assisted resin infusion of stacks of flax tapes conditioned according to section 2.2. Flexural three point bending tests in longitudinal direction were performed on a universal testing machine (Instron 4426) based on ASTM D790.

3 RESULTS AND DISCUSSION

3.1 Gel time curve and DSC

A typical gel time curve using 1.5 phr of curing agent and 1 phr of the copper based accelerator, is shown in Figure 2-A (see section 2.1 and 2.4 for the description of the components and the test method). Gel time is 2 minutes and the exothermic peak is observed at 130 °C and about 7 minutes for 30 mL volume. The system was designed to produce a rapid curing period in order to reduce the exposure of the pull-out test samples to room environmental conditions, and to have a sufficient working-life period to prepare the samples properly. Additionally, the exothermic process temperature is below the values reported for natural fibre thermal degradation (~190°C) [20, 21].

However, the amount of resin used for each pull-out test sample is very small (between 0.1 to 0.3 mL, depending on the embedded length), producing fast dissipation of the heat generated and needed by the curing process; which could provoke that the UP resin is not fully cured after solidification. So, with the purpose of investigating the level of cure of the samples, DSC analyses of cured samples at room conditions (Figure 2-B) and post cured samples at 80 °C for one hour (Figure 2-C), were conducted.

As it can be seen in Figure 2-B, the sample was still curing when the sample was heated up above 60 °C. This shows that the resin did not fully cure and that external heat was needed to complete the curing process. In contrast, the samples which were post-cured at 80 °C showed only a small reaction above 100 °C. This small peak is a specific characteristic of the copper-based UP resin, and it is not related to the curing process. Accordingly, all samples were cured at 80 °C to ensure complete curing of the resin.

3.2 Surface composition

The composition of technical flax fibres has already been reported by several researchers [22, 23], and consists of cellulose (71-82 %), hemicellulose (13-18 %), pectin (~2 %), lignin (2-3 %), and waxes (~1.7 %). Then, it is clear that the technical flax fibre bulk composition is mainly composed of cellulose. This same proportion of components is usually assumed for the fibre surface and for the study of flax fibre

composite interfaces and flax fibre wetting behaviour [24]. However, the composition of the fibre surface is not always the same as the bulk composition [13], and the stated assumption might be incorrect.

Relative element percentages, and decomposition of C1s peaks obtained by XPS for technical flax fibres are shown in Table 1. Cellulose content on the fibre surface was analysed by determining the oxygen-to-carbon atomic ratio (O/C), oxygen-to-carbon (linked to oxygen only) atomic ratio (O/C*), and the relative concentration of the C1 component. The first aspect deals with the fact that oxygen-to-carbon atomic ratios are different between cellulose and the other components, while the second and third aspects are concerned with the lack of C1 bonds in chemically pure cellulose within the C1s spectrum.

Table 1 shows that the surface of flax fibres that was analysed did not consist of cellulose. The O/C value of 0.15 is far different from that of reported for pure cellulose with a ratio of 0.83 [25]. Moreover, the O/C* (0.56) and C1/C (0.71) ratios are also different than the expected ratios of 1 and 0 respectively for pure cellulose. On the other hand, the O/C* ratio is close to 0.5, which is the reference for lignin [26]. However, the presence of other compounds such as lipids or pectin cannot be excluded, since the C1/C ratio is higher than the ratio for lignin (0.5) and some nitrogen was also detected, all of which should not be observed in pure cellulose. These results agree with earlier studies of cotton and bamboo fibres [13, 25], which showed that lignin, fatty acids, waxes and proteins, covered the cellulose in these fibres; the results also agree with studies that suggest that pectin is responsible for binding the cell wall layers together and is present in the middle lamella [27].

Concluding, the XPS results indicate that technical flax fibre surface may be homogeneously covered with lignin, pectin and some other molecules, but not with cellulose, within the measured depth of 5-10 nm.

3.3 Contact angle measurements and surface energy analysis

The measured advancing and receding contact angles of water, ethylene glycol, and diiodomethane on technical flax fibre, under different humidity conditions, as well as the calculated surface energy components, are shown in Table 2.

The standard deviations of the measured contact angles are large (although a careful procedure was followed during the test, see Section 2.3), which is in agreement with literature reviews attributing this large fluctuation to the influence of both chemical and morphological heterogeneity of the fibre surface [13, 28]; the former deals with the difference in wetting between natural fibre constituents such as lignin, cellulose and hemicelluloses, while the latter is concerned with surface roughness and differences in fibre perimeter. Additionally, technical fibres might be more susceptible to being affected by sorption, due to the mechanical extraction process of the fibre, which produces (local) separation of elementary fibres.

Although these fluctuations were observed, the contact angle results were able to show that humidity influences both advancing and receding contact angles. For water, the effect of humidity on advancing contact angles was small from 0% RH to 50% RH ($\sim 58^\circ$, see Table 2). However, advancing contact angle values increased to $69.5^\circ \pm 4.9^\circ$ at 70% RH and then decreased to $63.2^\circ \pm 6.7^\circ$ at 100% RH.

For Ethylene glycol, advancing contact angles were similar for 0%, 50%, and 100% RH ($\sim 50^\circ$, see table 2), but the wettability increased at 70% RH ($43.1^\circ \pm 6.8^\circ$). For the case of diiodomethane, there was no obvious trend, and contact angle values reached their maximum at 100% RH.

A possible explanation for this wetting behaviour could be related to the interaction of water in the environment with the natural fibre, and the possible migration of different extractives to the fibre surface at different humidity levels [29]. Furthermore, a similar wetting behaviour of water on a phospholipid DPPC layer deposited on glass (contact angles increasing while humidity increases and a sharp decrease at a high humidity level) was found by Chibowski et al. [30], who suggested that each thermodynamic state of the layer is characterized by a specific hydration level and a specific distribution of water molecules. Then, it is possible that a similar phenomenon could be happening, because flax fibre is a hygroscopic material,

and water molecules in the environment will always interact on the fibre surface and with the internal structure.

Since receding angles were significantly affected by liquid sorption (receding contact angles with diiodomethane were not possible to be measured, see Table 2), surface energy components analysis was based on advancing contact angles. The clearest change appeared at 100% RH, where the total surface energy reached the lowest value of 30.2 ± 1.9 mJ/m² due to reduction of the Lifshitz-van der Waals (LW) component. These results are in agreement with de Meijer et al. [31], who found that LW components reduce when moisture content increases for spruce and meranti wood. In general, there is no obvious trend that could link the variation of total surface energy with humidity, while the polar components (acid and base) remained relatively constant at different humidity levels. Only at 70% RH, a reduction of the basic components could be observed.

3.4 Pull-out test

By following the procedure described in 2.7.3, the measured and the theoretical maximum force (F_{max}), blue points and red dotted lines respectively in Figure 3, are plotted as function of the embedded length (l_e) for flax and UP resin systems under different RH conditions. The R^2 values for all the systems are close to one, which may confirm a good correlation of the measured and theoretical forces. The inserts show the residual plots for better analysing mild deviations of data from the model. The determined interfacial parameters are shown in Table 3.

The calculation of the interfacial parameters from pull-out tests for technical flax fibres was problematic. It is well known that natural fibres do not have a circular cross-section, the cross section changes along the fibre length and each fibre possesses a different perimeter [13]. Since the calculation of the pull-out interfacial parameters depends on the assumption of a perfect cylindrical body and the fitting of several maximum forces for different fibres of the same diameter, the results are approximations. However,

technical flax fibres of approximately the same fibre perimeter were carefully selected (see Table 3) in order to reduce the error related to perimeter and cross sectional shape variation.

All the obtained τ_d values are similar, only showing small variations. In the case of the fibres conditioned at 0% RH, a slightly higher practical adhesion was observed (see Table 3), which could be correlated with the slightly higher total surface energy at 0% RH (see Table 2). Since the fibre conditioning and preparation of the pull-out sample was performed at 0% RH and the pull-out test at 50% RH, it could be possible that the swelling of the fibre was producing some pressure against the solidified matrix, enhancing the τ_d value. At 50% RH, a flax fibre can have a weight gain of almost 3% if compared with fibres conditioned at 0% RH [8].

For the fibres conditioned at 50% RH, and post cured at 0% and 50% RH, the obtained τ_d values did not show a significant difference. These systems were prepared with the intention of evaluating if swelling or shrinkage of the fibre could be affecting the interfacial strength. The system that was post cured at 50% RH might not be affected by moisture sorption, since the fibres were also tested at 50% RH. On the other hand, the system that was post cured at 0% RH lost moisture and probably shrinkage could promote debonding, affecting negatively the interfacial strength. There is a slight reduction of interfacial shear strength from 10.3 MPa to 9.6 MPa at 50% and 0% RH respectively (post curing conditioning); however this small difference might not be conclusive.

The obtained τ_f values for the systems at 0% and 50% RH and post cured at 50%RH were similar (see Table 3), which was an expected result since no shrinkage was expected in any of these systems. However, the minimum τ_f values were obtained for the system conditioned at 70% RH and post-cured at 50% RH (2.1 MPa) and the system conditioned at 50% RH and post-cured at 0% RH (3.2 MPa), that could possibly be related to shrinkage phenomena produced by the loss of water content.

Regarding a direct correlation between the interfacial parameters determined from the pull-out test (Table 3) and the total surface energy or surface energy components (Table 2), this is not conclusive due to the standard deviation involved in the analysis. Contrary perhaps to expectations the results indicate that the interfacial shear strength and the surface energy were not severely affected by humidity variation. Although, slightly higher values of surface energy and shear strength for the samples at 0% RH were noticed.

It is likely that the insensitivity of the interface to moisture is related to its chemical composition. The fibre surface was shown before to be rich in lignin, which is a relatively hydrophobic ingredient. Also, the surface energy results suggest a surface of moderately hydrophobic nature. These facts could help explain the insensitivity of the interphase to moisture.

3.5 Composite performance (3 PBT)

At the composite level, the effect of high humidity is more evident as can be seen in Table 4. At 100% RH during manufacture, the flexural strength decreased from 230 MPa to 188 MPa, and the flexural Young's modulus from 20 GPa to 15 GPa, representing a reduction of 18% and 25% respectively when samples were tested after 24 hours of being manufactured. However, at the high level of environmental humidity (100%) during manufacture, flax fibre/cobalt based unsaturated polyester resin composites were not able to cure and showed a reduction of mechanical properties of the order of 100% [11]. In the same fashion, Zhang et al. [8], observed a 35% and 39% loss of flexural strength and Young's modulus respectively at only 90% RH during manufacture, for flax fibre/cobalt based UP resin composites. Because the samples are conditioned in standard room conditions (22°C and 50% RH) for only 24 hours after manufacture and before testing, they will still largely contain the humidity levels imposed during manufacture. Therefore, at first sight, the loss in properties for 100% RH, could largely be attributed to moisture reducing the constituent properties, rather than some detrimental effect of humidity during manufacture on material integrity.

A composite material is a three phase system (fibre, matrix, and interphase), and the effect of humidity in each phase could affect its mechanical performance. As it has been shown before, surface energy and interfacial shear strength were not drastically affected by humidity, showing that the physical and mechanical properties of the interphase remained relatively stable. This was confirmed by the transverse 3 point bending tests, showing that the transversal mechanical properties were similar at 0% and 100% RH during manufacture (see Table 4), corroborating the pull-out analysis.

The effect of humidity (up to 90% RH) on the mechanical properties of elementary natural fibres (hemp) has already been reported in literature [32]. According to these studies, the Young's modulus increases with humidity content, while tensile strength increases until 70% RH. Beyond this point, the strength slightly reduces. It was suggested that water could penetrate the fibre network, softening the amorphous components' (lignin, pectin, hemicellulose, etc.) rigidity and promoting the realignment of cellulose nanofibrils in the loading direction, producing the increase of stiffness at higher strains. However, at certain high moisture content threshold, the excess of humidity leads to the formation of layers of water molecules on top of already absorbed water molecules (bound water), making the softening effect less dominant, and producing the reduction of strength.

For the case of technical flax fibres, these become less stiff at higher humidity, but present larger strain to failure [7]. Regarding the strength behaviour, there is an increase up to a certain moisture level due to the improved ductility [33]. At very high humidity, the main components at the interface (lignin and pectin, according to the XPS analysis) of the elementary fibres may start to soften and probably dissolve, producing a possible technical fibre defibrillation, and a reduction in longitudinal strength. In the composite, for relatively fine technical flax fibres, mechanical properties may be controlled by the elementary fibres [34]. Then, strength may keep rising until high humidity levels, until lignin and pectin are softening or dissolving, and lowering fibre-matrix interface strength.

On the other hand, if only the matrix is taken into account, cobalt based UP is clearly affected by humidity content during cure. The latter is related to the nature of cobalt, which is prone to hydrolysis under the influence of water and becomes unreactive for the curing process. A previous publication showed that even at 2% of water content during cure, a cobalt based UP system has difficulties to cure (partial curing), and at 4% does not cure at all. Moreover, composites manufactured with fibres (pre-saturated with moisture, 100% RH) in combination with a cobalt based UP system, were not able to cure neither solidify [11]. In contrast, copper based UP resin was able to cure under 100% RH and to reach efficiency factors higher than 90% for both strength and Young's modulus once re-conditioned to standard environmental conditions, showing a very low sensitivity to presence of water during curing.

However, after 6 months re-conditioning to standard 50% RH environment, the mechanical properties of the samples in this study remained similar to the levels 1 day after manufacture, although a slight recovery of mechanical properties could be appreciated in the case of composites manufactured at 100% RH. Accordingly, there seems to be some detrimental effect of moisture during manufacture on the composite mechanical properties of flax/UP resin composites and this effect is largely irreversible. Since in table 4, the transverse modulus, which is strongly controlled by matrix modulus, is hardly affected by the moisture level and it is the fibre dominated longitudinal properties which are most affected by the moisture, it can be concluded that there is some detrimental effect of high levels of moisture during cure on the fibre mechanical performance.

4 CONCLUSIONS

As was shown in Section 3.2 (XPS analysis), the fibre surface is mainly composed of amorphous polymers (lignin, pectin, hemicelluloses) and possibly waxes. Although this layer might be susceptible to water absorption since it is the area that is more exposed to the environment, both its surface energy and the interfacial shear strength remained relatively constant at different humidity levels (see Section 3.3 and 3.4). However, when the mechanical properties of the composite at 0% and 100% RH are compared

(Section 3.5), there is a reduction in longitudinal strength which may be related to the decrease of the fibre mechanical properties due to softening and possible dissolution of the interface between elementary fibres.

Regarding the UP resins, when copper and cobalt based systems are compared, the former exhibits a very low sensitivity to the presence of water, being able to cure at high levels of humidity (100% RH at 20 °C, and 70% RH at 80°C). Under the same conditions (100% RH at 20 °C), cobalt based resin composites are not able to cure, showing no mechanical properties.

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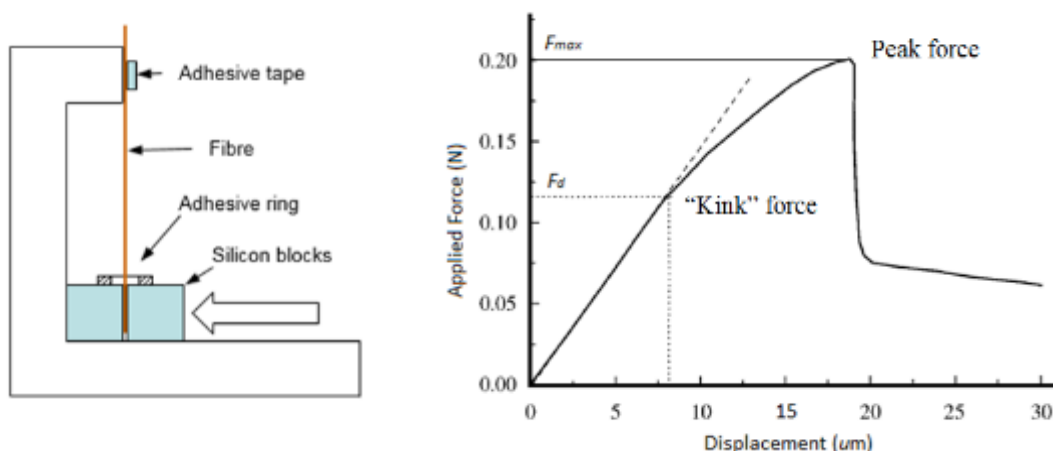


Figure 1. Device for preparation of pull-out samples (Left), and a pull-out test force-displacement curve (Right).

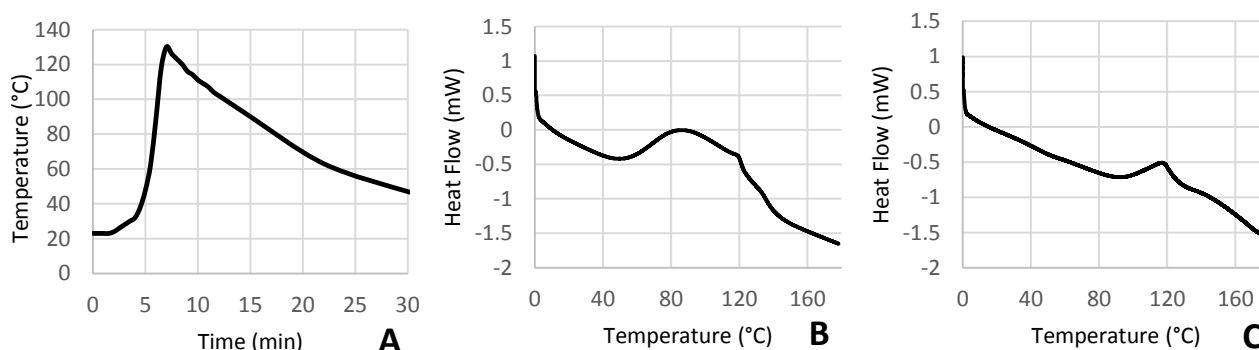


Figure 2. Gel time curve (A) and differential scanning calorimetry (DSC) analysis of UP resin after curing (B), and after post curing (C).

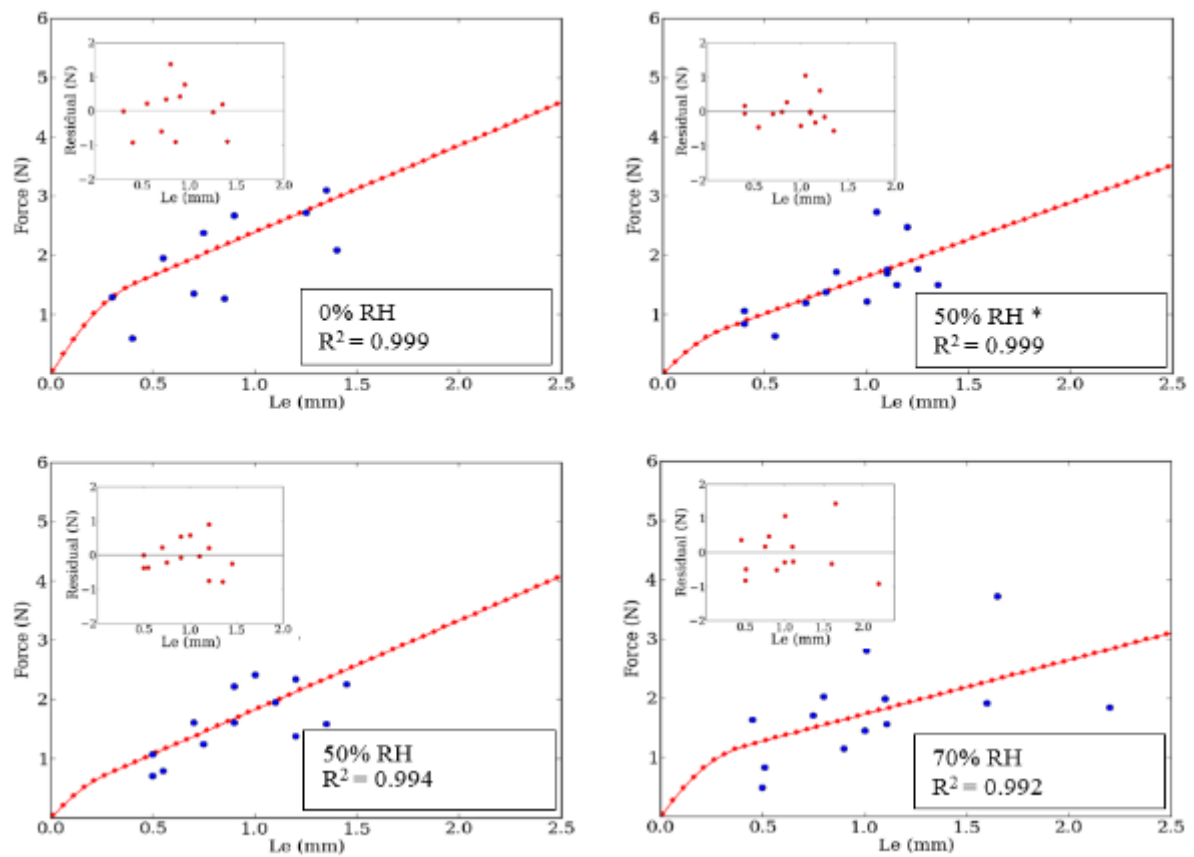


Figure 3. Experimental plot of the F_{max} versus the embedded length for copper-based UP resin/flax fibre systems, and their theoretical fits. Experimental plot in blue dots and its theoretical fit in red dotted lines. * The sample was post cured at 0% RH.

C (%)	O (%)	N (%)	Si (%)	O/C	O/C*	C1/C	Binding energy (eV)			
							284.8	286.3	287.6	289.0
							C1 (%)	C2 (%)	C3 (%)	C4 (%)
							(C-(C,H))	(C-O,N)	(C=O, O-C-O)	(O-C=O)
85.1 ±1.1	12.8 ±0.6	1.6 ±0.2	0.8 ±0.1	0.15	0.56	0.71	60.6 ±1.2	18.2 ±0.9	4.8 ±0.6	1.5 ±0.2

Table 1. Relative element percentages (excluding hydrogen), and decomposition of C1s peaks obtained by XPS on flax technical fibres. (*) Carbon linked to oxygen only.

Table 2. Contact angles of test liquids on flax technical fibres; and their surface energy components. Fibres were tested at a speed of 1 mm/min. Adv: Advancing contact angles, Rec: Receding contact angles, RH: Relative humidity, WT: Water, EG: Ethylene glycol, DIO: Diiodomethane, γ^{LW} : Lifshitz-van der Waals component, γ^+ : Acid component, γ^- : Basic component.

RH (%)	WT		EG		DIO		Surface Energy Components			
	Adv (°)	Rec (°)	Adv (°)	Rec (°)	Adv (°)	Rec (°)	γ^{tot} (mJ/m ²)	γ^{LW} (mJ/m ²)	γ^+ (mJ/m ²)	γ^- (mJ/m ²)
0	59.8 ±6.8	38.1 ±4.5	50.3 ±7.6	29.8 ±5.5	45.5 ±6.6	--	37.4 ±4.7	34.1 ±3.4	0.2 ±0.4	11.0 ±4.0
50	58.8 ±7.2	29.8 ±5.5	53.6 ±3.7	34.3 ±3.3	59.0 ±6.1	--	32.4 ±2.1	29.2 ±1.5	0.2 ±0.2	14.3 ±1.3
70	69.5 ±4.9	35.2 ±8.9	43.1 ±6.8	28.7 ±3.8	49.8 ±5.8	--	37.8 ±2.7	34.4 ±2.2	0.5 ±0.4	5.8 ±2.3
100	63.2 ±6.7	--	53.1 ±6.8	--	65.0 ±6.0	--	30.2 ±1.9	25.7 ±1.4	0.4 ±0.2	12.4 ±1.2

Table 3. Interfacial parameters for UP resin and technical flax fibre as substrate.

Group	Fibre conditioning RH (%)	Post Curing RH (%)	τ_d (MPa)	τ_f (MPa)	Average fibre diameter (µm)
1	0	0	13.6	3.5	133±8
2	50	0	9.6	3.2	112±9
3	50	50	10.3	3.9	114±7
4	70	70	11.7	2.1	129±7

Table 4. Longitudinal and transversal strength in 3 PB of unidirectional flax fibre/UP resin composites for different humidity conditions and the efficiency factor of longitudinal flexural strength and modulus; RH conditions for fibres during manufacturing; after manufacturing composites were conditioned for 1 day or for 6 months in standard room conditions.

Time	RH (%)	Longitudinal				Transversal	
		Young's modulus (GPa)	Efficiency factor (%)	Strength (MPa)	Efficiency factor (%)	Young's modulus (GPa)	Strength (MPa)
24 hours	0	20.3±0.3	92	230.7±5.6	95	2.3±0.2	16.4±0.6
	100	15.3±1.1	69	188.6±5.8	78	2.1±0.4	17.5±2.6
6 months	0	19.8±0.5	90	225.9±2.9	93	2.2±0.2	16.3±0.3
	100	16.3±0.6	74	197.8±2.1	82	2.1±1.2	16.9±0.6